# Ground-state properties of cubic C–BN solid solutions

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**Abstract.** The *ab initio* calculations of the ground-state properties of cubic C–BN solid solutions are presented for the first time to our knowledge. The Löwdin perturbation technique has been used in the *ab initio* LMTO–ASA method to calculate the total energy, the equilibrium lattice constant, the bulk modulus and its pressure derivative and the formation energy of mixed crystals of cubic BN and diamond. The calculated results indicate that the solid solution between C (diamond) and cubic BN is nonideal, with the equilibrium lattice constants larger than the predicted values of ideal mixing (Vegard's law) and the positive energies of formation. The bulk moduli of BN-rich $(BN)_x(C_2)_{1-x}$ ($x > 0.5$) are lower than those of diamond, the value of ideal mixing and even cubic BN. This anomalous behaviour is consistent with the nonideal expansion of the equilibrium lattice constant. The calculated results are in good agreement with the recent experimental measurements by Knittle *et al* 1995 *Phys. Rev.* B **51** 12149.

## 1. Introduction

There are many applications for hard materials in high-performance engineering applications. Diamond and cubic boron nitride (c-BN) have recently received considerable attention because of the extreme values of their properties such as hardness, thermal conductivity, elastic constants and band gaps [1], and their promising material properties for abrasives, heatsinks, protective coatings and wide band-gap semiconductor applications. Therefore, the synthesis of these difficult-to-obtain materials has stimulated great interest and has been increasingly studied in recent years [2–4]. Several groups have tried to synthesize these and related materials using different growth techniques such as energetically enhanced (plasma, hot filament, microwave) chemical vapour deposition (CVD) [2], laser ablation [3], and ion-beam techniques [4]. Since the physical properties of cubic BN are very similar to those of diamond, cubic BN films are candidate substitutes for the envisioned applications for diamond films. Moreover, the small lattice mismatch between cubic BN and diamond suggests that cubic BN may indeed be an attractive substrate for epitaxial diamond-film growth, and would be the natural candidate for heterojunctions with diamond [5–7]. For the extreme values of diamond and c-BN, there are several theoretical studies on relevant heterojunctions or superlattice structures and the properties of mixed crystals of diamond and c-BN. For example, the electronic structure of diamond/sphalerite BN interfaces and superlattices were presented by Lambrecht and Segall [5] and Pickett [7]; the anomalous band-gap behaviour and phase stability of c-BN–diamond

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alloys were studied by Lambrecht and Segall [8]; the valence band offsets of C/BN strained heterojunctions and $C/(BN)_x(C_2)_{1-x}$ and $BN/(BN)_x(C_2)_{1-x}$ were studied by Zheng *et al* [9].

For the hexagonal phases of carbon and BN, namely, graphite and h-BN, the structures are more thermodynamically stable than diamond and c-BN at normal pressure. Mixed C–BN layered hexagonal phases have been synthesized by a number of groups [10–17], and studied theoretically by Liu *et al* [18]. Starting from the layered hexagonal mixed crystals, Badzian has synthesized mixed crystals of diamond and c-BN by a high-pressure high-temperature phase-transformation technique [10]. Recently, Knittle *et al* [19] reported the synthesis of several cubic C–BN solid solutions using the laser-heated diamond cell. They measured the effect of composition on the lattice parameters and vibrational frequencies of samples across the C–BN solid solution, and also measured the isothermal bulk modulus of $C_x B_x N_x$ ($x \sim 0.33$).

In this paper, we present results of total energy calculations for five ordered structures of $(BN)_n(C_2)_{4-n}$ ($n = 0, 1, 2, 3, 4$) by means of the local-density-functional theory and the linear-muffin-tin-orbital (LMTO) band-structure method in the atomic-sphere approximation. We calculate the ground-state properties of $(BN)_n(C_2)_{4-n}$. These include the zero-pressure lattice constant, bulk modulus and cohesive energy. We also determine the statistically averaged properties of the disordered alloys by a cluster expansion, which is a generalization of the Connolly–Williams approach [20].

## 2. Methods of calculation

The total energies of the five ordered structure alloys $(BN)_n(C_2)_{4-n}$ are calculated by means of the LMTO–ASA method with the Löwdin perturbation technique [21]. Among the five ordered structures ($n = 0, 1, 2, 3, 4$), the $n = 0$ element (C) and $n = 4$ compound (BN) have diamond and zinc-blende (ZB) structures respectively. The $n = 2$ compound has the CuAu structure (L10), and $n = 1$ and 3 compounds have Luzonite (L12) structures. In order to provide an adequate description of the charge density and potential in interstitial regions, empty spheres (equal to the number of atoms in a unit cell) are added at suitable sites, while preserving the crystal symmetry. The ratio of radii for B, N and C atoms and the empty sphere are 1:1:1:1. The special-$k$-point method [22] is adopted for the summation over the Brillouin zone.

## 3. The ground-state properties of cubic C–BN solid solutions

### 3.1. The equilibrium lattice constants

The results of total energies $E_{tot}$ (eV) as a function of $V/V_0$ are obtained by the above method. The equilibrium lattice constants obtained from total-energy calculation for C and cubic BN are listed in table 1. The experimental data and other calculated results are also listed in table 1. The lattice constants of C and BN presented here are all between those of other calculations and experiments. The fact that our lattice constants are slightly larger than other calculations is mainly due to the Löwdin perturbation scheme used in our calculation. They are also little underestimated compared to experiment because of the neglect of the so-called combined-correction term in our total-energy calculations, but the differences between the experimental data and our results are very small, i.e., only 0.005 Å (0.1%) for C and 0.006–0.007 Å (0.17%) for cubic BN.
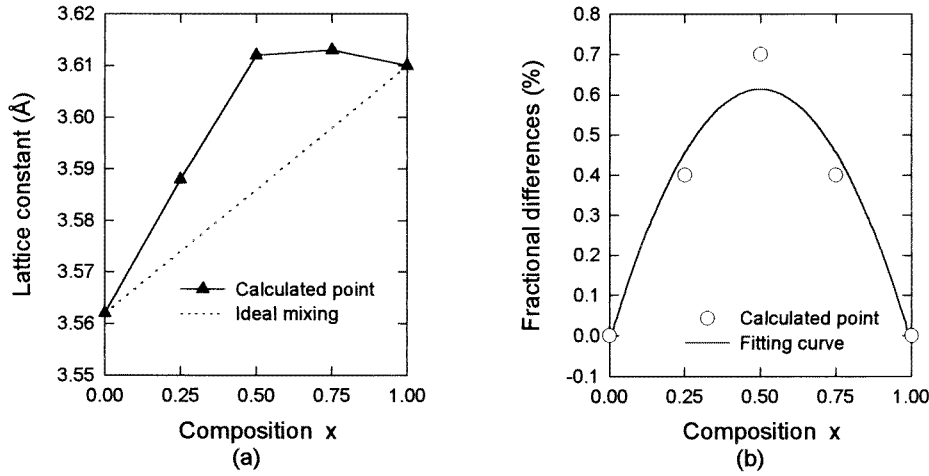
The calculated lattice constants for five ordered structure alloys $(BN)_n(C_2)_{4-n}$ ($n = 0, 1, 2, 3, 4$) compared with lattice constants of ideal mixing solid solutions are listed in table 2 and shown in figure 1. From figure 1(a), one can see that the calculated lattice constants are

**Table 1.** Calculated lattice constants for C and BN compared with the experiments and other calculations.

|  | $a_0$ (Å) |
|---|---|
| **C** | |
| Present calc. | 3.562 |
| Other calc. | 3.561 [23], 3.55 [24], 3.53 [5], 3.56 [26, 27] |
| Expt | 3.567 [19, 25, 30] |
| **BN** | |
| Present calc. | 3.610 |
| Other calc. | 3.58 [5], 3.606 [31] |
| Expt | 3.617 [19], 3.616 [30] |

**Table 2.** Calculated lattice constants, lattice constants of ideal mixing solid solutions and the difference between them for five ordered structure alloy $(BN)_n(C_2)_{4-n}$ ($n = 0, 1, 2, 3, 4$). All units are in angströms.

|  | Calculated lattice constants $a_0$ | Lattice constants of ideal mixing solid solutions $a_i$ | Differences $a_0 - a_i$ | Fractional differences $(a_0 - a_i)/a_i$ (%) |
|---|---|---|---|---|
| C | 3.562 | 3.562 | 0 | 0 |
| $(BN)(C_2)_3$ | 3.588 | 3.574 | 0.014 | 0.4 |
| $(BN)(C_2)$ | 3.612 | 3.586 | 0.026 | 0.7 |
| $(BN)_3(C_2)$ | 3.613 | 3.598 | 0.015 | 0.4 |
| BN | 3.610 | 3.610 | 0 | 0 |



**Figure 1.** (a) The calculated lattice constants (solid triangles) and lattice constants of ideal mixing solid solutions (dashed line) for five ordered structure alloys $(BN)_n(C_2)_{4-n}$ ($n = 0, 1, 2, 3, 4$). (b) The differences between calculated lattice constants and lattice constants of ideal mixing solid solutions (open circles are calculated points, and solid line is fitting curve). All units are in angströms.

larger than those of ideal mixing between diamond and BN. The differences are also listed in table 2 and shown in figure 1(b). According to Vegard's law, the lattice constants of the ideal mixing $(BN_n)(C_2)_{4-n}$ solid solution can be written as $a(n) = (n/4)a(BN) + (1 - n/4)a(C_2)$.

The departure from Vegard's law is the largest for $(BN)(C_2)$ ($x = 0.5$ for $(BN)_x(C_2)_{1-x}$). The anomalous behaviour of lattice constants indicates that the cubic C–BN compounds are nonideal solid solutions, such that the incorporation of BN into the cubic diamond lattice results in expansion of the crystallographic unit cell relative to Vegard's law. The calculated results are in good agreement with recent experimental data by Knittle *et al* [19]. The nonideality of the molar volumes in the cubic C–BN system can be described with a standard mixing model where the excess volume term is given by $\Delta V^{KS} = x(1 - x)(\delta W^G/\delta P)$ [19, 32, 33]. Here, $x$ and $(1 - x)$ are the mole fractions of cubic BN and C, and $W^G$ is the interaction (or Margules) parameter. We obtain the $\delta W^G/\delta P$ for the three ordered structures of $(BN)(C_2)_3$, $(BN)(C_2)$ and $(BN)_3(C_2)$ as 0.22, 0.30, and 0.23 J MPa$^{-1}$ respectively, which is about twice the values obtained from experimental measurements [19] ($0.13 \pm 0.02$ J MPa$^{-1}$). The maximum deviation from ideality is ~2% in volume, which is also twice that of the experimental values [19]. The slightly larger values might be due to the fact that our results are obtained from ordered structures, whereas the experimental data are obtained from disordered solutions. In disordered alloys, statistical averaging will lead to a decrease of nonideality.

## 3.2. Isothermal equation of state

From the results of the total energy calculation, the isothermal equation of state for $(BN)_n(C_2)_{4-n}$ can be obtained, which is shown in figure 2. The pressure can be expressed as the function of volume $(V/V_0)$. The relationship of the strain $V/V_0$ under the same pressure among the different compositions of solid solution $(BN)_n(C_2)_{4-n}$ can be obtained as

$$(V/V_0)_{diamond} < (V/V_0)_{(BN)(C_2)_3} < (V/V_0)_{(BN)(C_2)} < (V/V_0)_{(BN)} < (V/V_0)_{(BN)_3(C_2)}$$
$$\text{where } P > 0$$

and

$$(V/V_0)_{diamond} > (V/V_0)_{(BN)(C_2)_3} > (V/V_0)_{(BN)(C_2)} < (V/V_0)_{(BN)} > (V/V_0)_{(BN)_3(C_2)}$$
$$\text{where } P < 0.$$

The above relation shows that $(BN)_n(C_2)_{4-n}$ ($n - 1, 2, 3, 4$) can be compressed or expanded more easily than diamond under the same pressure. Although the $P–V$ curve of $(BN)(C_2)_3$, which contains 75% diamond, is higher than that of BN, that of $(BN)(C_2)$, which contains 50% diamond, is only slightly larger than that of BN, while that of $(BN)_3(C_2)$, which contains 25% diamond, is even lower. (See figure 2 and the inset figure.) These calculated results are in good agreement with experimental work (see figure 3 of [19]). In their work, Knittle *et al* found that the equation of state for $C_x(B_xN_x)$ ($x \sim 0.33$) (which is the same as $(BN)_{0.67}(C_2)_{0.33}$ in this work) was lower than that for BN. The theoretical results and the experimental results show that C–BN solid solutions are nonideal, and the conclusions are consistent with the nonideal expansion for the cubic C–BN lattice constants.

## 3.3. Bulk modulus

Hardness is one of the most important issues in the study of the cubic C–BN solid solution. The bulk modulus is often regarded as a measure of the hardness of materials. Based on the total-energy results, we obtain the bulk modulus as follows:

$$B = V \frac{d^2 E_{tot}}{dV^2} \tag{1}$$

where $B$ is the bulk modulus, $V$ is the unit cell volume and $E_{tot}$ is the total energy. The calculated bulk moduli $B_0$ and their pressure derivatives $B_0'$ for C and BN are compared with
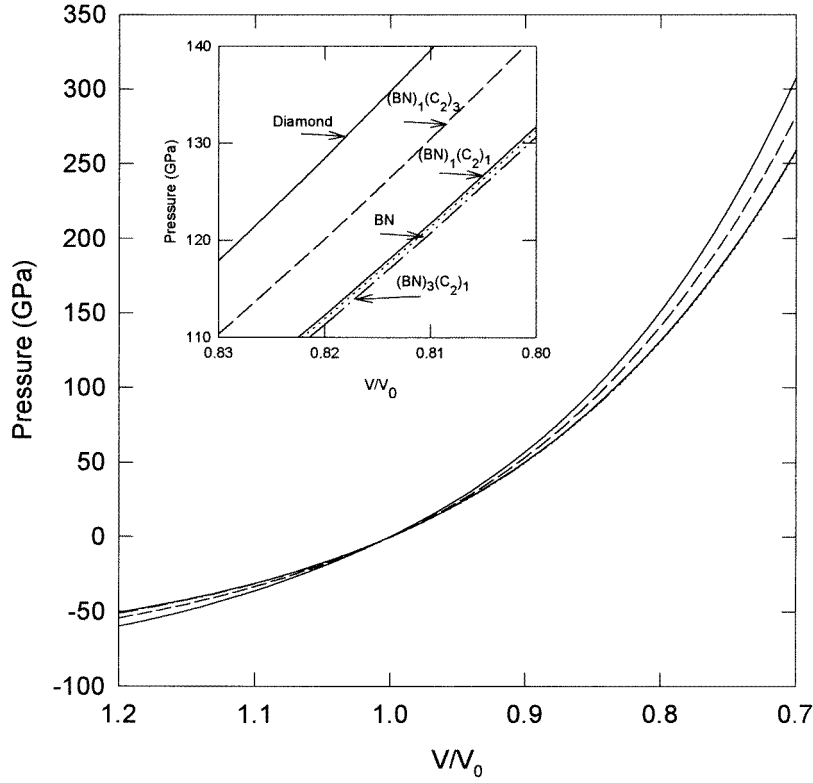
**Figure 2.** Calculated pressure–volume data for $(BN)_n(C_2)_{4-n}$. The curves from top to bottom are the isothermal equations of state for diamond, $(BN)(C_2)_3$, $(BN)(C)_2$, BN and $(BN)_3(C_2)$. (Also shown as the inset figure.)

the experimental and other calculated results in table 3. Equation (1) is a direct calculation from total energy results. There are several other methods to calculate bulk modulus. One important method is to calculate the bulk modulus of each structure by fitting the total energy–volume to the Birch–Murnaghan equation of state [37],

$$E_{tot}(V) = \frac{B_0 V}{B_0'} \left[ \frac{(V_0/V)^{B_0'}}{B_0' - 1} + 1 \right] + \text{constant} \tag{2}$$

where $B_0$ and $B_0'$ are the bulk modulus and its pressure derivative at the equilibrium volume $V_0$. Note that equation (1) can be derived from equation (2), and the differences between the results obtained by equations (1) and (2) are very small, so we have listed the results from equation (1). Cohen had developed a simple empirical formula [38] for the bulk moduli of diamond and zinc-blende solids using scaling arguments for the relevant energy and volume. It can be expressed as [39],

$$B_0 = \frac{N_c}{4} \frac{(1972 - 200I)}{d^{3.5}} \tag{3}$$

where $N_c$ is the coordination number. An empirical ionicity parameter $I = 0, 1$ and 2 for group IV, III–V and II–VI solids, respectively, accounts for the reduction in $B_0$ arising from increased charge transfer. For tetrahedral systems, $N_c = 4$; otherwise $N_c$ is the average coordination number.

**Table 3.** Calculated bulk moduli and their pressure derivatives for C and BN compared with experiments and other calculations. (The values in brackets are predicted from the empirical formula.)

|  | $B_0$ (GPa) | $B_0$ |
|---|---|---|
| **C** |  |  |
| Present calc. | 446 (433) | 3.45 |
| Other calc. | 438 [23, 26, 27], 470 [24], 480 [5] | 3.5 [23, 26, 27], 4.2 [24], 3.6 [5] |
| Expt | 443 [25], 442 [28], 545 [29] | 4.0 [25] |
| **BN** |  |  |
| Present calc. | 392 (371) | 3.79 |
| Other calc. | 412 [5], 367 [31] | 3.6 [5] |
| Expt | 290 [5][a], 465 [34][a], 369 [35] |  |

[a] From estimated elastic constants.

**Table 4.** Calculated bulk moduli, their pressure derivatives from total energy results (equation (1)), bulk moduli from empirical formula (equation (3)), and the differences from ideal mixing.

|  | Equation (1) | | | | Equation (3) | | |
|---|---|---|---|---|---|---|---|
|  |  |  | Differences from ideal mixing | |  | Differences from ideal mixing | |
|  | $B_0$ | $B_0'$ | $B_0 - B_i$ | $(B_0 - B_i)/B_i$ (%) | $B_0$ | $B_0 - B_i$ | $(B_0 - B_i)/B_i$ (%) |
| C | 446 | 3.45 | 0 | 0 | 433 | 0 | 0 |
| $(BN)(C_2)_3$ | 416 | 3.84 | $-16.5$ | 4 | 411 | $-6.5$ | 2 |
| $(BN)(C_2)$ | 391 | 3.85 | $-28$ | 8 | 391 | $-11$ | 3 |
| $(BN)_3(C_2)$ | 389 | 3.81 | $-16.5$ | 4 | 380 | $-6.5$ | 2 |
| BN | 392 | 3.79 | 0 | 0 | 371 | 0 | 0 |

To compare the results of bulk moduli by different methods, we also use equation (3) (based on calculated lattice constant results) to calculate $B_0$ for $(BN)_n(C_2)_{4-n}$ which are shown in table 4.

From table 3, it can be seen that our calculated bulk modulus of 446 GPa for diamond is close to the experimental value of 442 GPa, and lower than a previous LMTO result [5] but higher than the calculated values of [26] and [27]. But the results from the empirical formula are smaller than the values from total-energy calculation for diamond and BN. Due to the high bulk modulus of diamond, the addition of diamond to a BN crystal should increase the hardness of the alloys. However, our calculated results show that the bulk moduli of the ordered alloys $(BN)_n(C_2)_{4-n}$ ($n = 1, 2, 3$) (which are shown as solid circles in figure 3) are lower than the interpolated values between diamond (446 GPa) and BN (392 GPa) (shown as the dashed line in figure 3). The bulk moduli of $(BN)_3(C_2)$ (containing 25% diamond) and $(BN)(C_2)$ (containing 50% diamond) are even lower than that of BN. Although the bulk modulus value of $(BN)(C_2)_3$ (which contains 75% diamond) is higher than that of BN, the difference (24 GPa) is only 44% of the difference between diamond and BN (54 GPa). The bulk moduli from the empirical formula (equation (3)) are found to be lower than those from total-energy calculation (equation (1)). The results also show that bulk moduli of the ordered alloys are lower than that of ideal mixing.
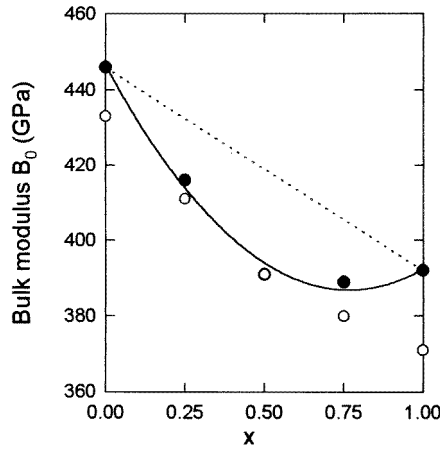
**Figure 3.** The total-energy calculated bulk moduli and those predicted from the empirical formula for ordered alloys $(BN)_n(C_2)_{4-n}$ as well as that of ideal mixing.

## 4. Properties of disordered alloys

The properties of the disordered alloys, such as the energy of formation, can be expanded in a cluster expansion (total energy expansion). One can calculate the probability distribution of the tetrahedral clusters from the minimization of the free energy within Kikuchi's cluster variation method (CVM) [8, 40, 41]. By using a random distribution for statistical averaging, the energy of formation of disordered alloys can be obtained as follows [8]:

$$E_{form}(x) = \sum_{n=0}^{4} P_n(x) E_{form}^n \qquad (4)$$

where $E_{form}(x)$ is the energy of formation of disordered alloys, and $E_{form}^n$ is the energy of formation of each of the above five ordered structures, $P_n(x)$ is the statistical weight, which is the probability that the $n$th short-range ordered structure occurs in the alloy. It can be expressed as

$$P_n(x) = \binom{4}{n} x^n (1-x)^{4-n}. \qquad (5)$$

Using this approach, the energy of formation of disordered alloys can be obtained as

$$E_{form}(x) = 0.6x^4 - 1.28x^3 - 0.78x^3 + 1.4x. \qquad (6)$$

The energies of formation of disordered alloys are lower than those of ordered alloys (as seen in figure 4). The statistical averaging simply leads to renormalization by a factor of about $3/4$.

## 5. Conclusion

In this paper, the study of ground-state properties of cubic C–BN solid solutions from first-principles calculations are presented. The total energy, equilibrium lattice constant, bulk modulus and its pressure derivative and formation energy of mixed crystals of diamond and cubic BN have been calculated by the *ab initio* LMTO–ASA method with Löwdin perturbation technique. The calculated results indicate that the solid solution between C (diamond) and cubic
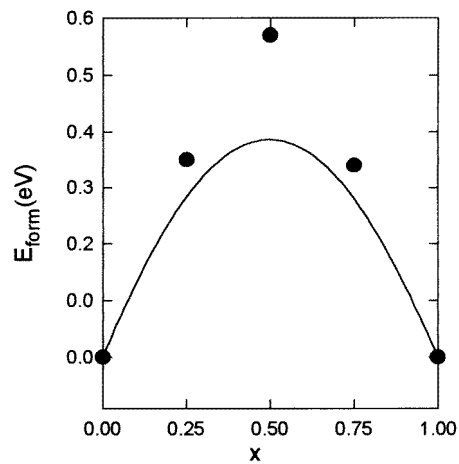
**Figure 4.** The calculated energy of formation for ordered structure (solid circles) and disordered alloys (solid line).

BN is nonideal, with equilibrium lattice constants larger than predicted values for ideal mixing (Vegard's law) and positive energies of formation. The bulk moduli of BN-rich $(BN)_x(C_2)_{1-x}$ ($x > 0.5$) solid solutions are lower than those of diamond, cubic BN and the value of ideal mixing. This behaviour is consistent with the nonideal expansion of the equilibrium lattice constant. The calculated results are in good agreement with experimental measurements.

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